Recent Theoretical Investigations of Inertial Effects in Dielectric Relaxation

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INTRODUCTION

It is well known that the 1913 Debye theory cannot adequately describe dielectric absorption. Indeed at high frequencies it leads to a constant absorption coefficient, with the implication that all polar liquids would be opaque throughout the infra-red and optical regions. It is generally accepted that this absurd result is due, at least in part, to the neglect of the inertia of the polar molecules.

The problem of dielectric relaxation involves the study of the rotational Brownian motion of a polar molecule in a non-polar solvent consisting of particles whose dimensions are small compared with those of the polar molecule. In the present study the interaction between the polar molecules themselves is neglected. Brownian motion including inertial effects may be investigated by Langevin equations or, equivalently, by phase space diffusion equations. We report on recent investigations carried out by these two methods.

DIFFUSION EQUATION INVESTIGATIONS

Relaxation effects may be described in terms of the complex polarizability $\alpha(\omega)$ due to a field of frequency $\omega/2\pi$. If in a relaxation process the dipole axis of the polar molecule makes an angle $\theta(t)$ with its direction at time t = 0 when the process commences, then the autocorrelation function $\langle \cos\theta(t) \rangle$ of $\cos\theta(t)$ and the complex polarizability are related to each other by

$$\alpha(\omega) = \alpha(0)\left[1 - i\omega \int_0^\infty \langle \cos\theta(t) \rangle e^{-i\omega t} dt\right]. \qquad (1)$$

Sack[1] calculated $\alpha(\omega)$ by integrating over phase space $\cos\theta(t)$ multiplied by the distribution function that satisfies the relevant diffusion equation. As models for the polar molecule he took a disk whose axis of rotation is in a fixed direction, a rotating needle and a rotating sphere, the last model being the most difficult to treat. After very lengthy calculations he expressed $\alpha(\omega)$ for each model as a continued fraction.

Since continued fractions are connected with three-term recurrence relations and since recurrence relations can often be neatly expressed as matrix equations, the diffusion equation study of the rotating sphere has been performed by a matrix method[2]. If the moment of inertia about a diameter is I and if the frictional couple that retards the rotation is β times the angular momentum about a diameter, we write

$$\frac{kT}{I\beta^2} = \gamma \quad , \quad \frac{\omega}{\beta} = \omega' \qquad (2)$$

Then the matrix method allows $\alpha(\omega)/\alpha(0)$ to be expressed as a power series in γ:

$$\frac{\alpha(\omega)}{\alpha(0)} = \frac{2\gamma}{i\omega'(i\omega'+1)} - \frac{2\gamma^2}{i\omega'(i\omega'+1)^2}\left\{\frac{2}{i\omega'} + \frac{3}{i\omega'+2}\right\} + \cdots \qquad (3)$$

The series has been continued up to terms proportional to γ^6.

The absorption coefficient is

$$\frac{\sqrt{2}\,\omega}{c}\sqrt{|\varepsilon(\omega)| - \varepsilon'(\omega)}\,,$$

where $\varepsilon(\omega) \equiv \varepsilon'(\omega) - i\varepsilon''(\omega)$ is defined in the absence of dipole-dipole interactions by

$$\frac{\varepsilon(\omega)-1}{\varepsilon(0)-1} = \frac{\alpha(\omega)}{\alpha(0)}.$$

As ω tends to infinity, the absorption coefficient deduced from (3) is proportional to ω^{-2}. The difficulty of the constant absorption coefficient is thus eliminated. The same may be shown to be true when the rotating needle is treated by the matrix method.

On account of (1), results for dielectric relaxation are often expressed by the value of $\langle \cos\theta(t)\rangle$. For nuclear magnetic relaxation one may need $\langle P_2(\cos\theta(t))\rangle$, where P_2 is the Legendre polynomial. In order to keep the results as general as possible we shall study $\langle Y_{jm}(\theta(t),\phi(t))\rangle$, where Y_{jm} is the spherical harmonic.

LANGEVIN EQUATION INVESTIGATIONS

The diffusion equation method suffers the disadvantage of requiring the solution of a second order partial differential equation. In order to use a Langevin equation we take a polar molecule whose shape has no special symmetry and through its centre of mass choose coordinate axes in the directions of the principal axes of inertia. Let I_x, I_y, I_z be the principal moments of inertia and $\omega_x, \omega_y, \omega_z$ the components of angular velocity. According to Euler's discussion of rotating coordinate systems the time rate of change of the x-component of angular momentum of the body is

$$I_x \dot{\omega}_x - (I_y - I_z)\omega_y \omega_z .$$

This is equal to the sum of the moments of the driving couple caused by the thermal motion of the surrounding particles and of the retarding couple about the x-axis. We assume that the latter is $-I_x \beta_x \omega_x$, where β_x is a friction constant. This assumption seems to be reasonable for many polar molecules. The random driving couple is written $(I_x A_x(t), I_y A_y(t), I_z A_z(t))$, where

$$\langle A_x(t)\rangle = 0 \quad , \langle A_x(t_1) A_y(t_2)\rangle = 0,$$

$$\langle A_x(t_1) A_x(t_2)\rangle = \frac{2\beta_x kT}{I_x}\delta(t_1 - t_2), \quad \text{etc.},$$

$\delta(t_1 - t_2)$ being a Dirac delta-function. The Euler-Langevin equations of motion are thus

$$\begin{aligned} \dot{\omega}_x - \frac{I_y - I_z}{I_x}\omega_y\omega_z &= -\beta_x\omega_x + A_x(t) \\ \dot{\omega}_y - \frac{I_z - I_x}{I_y}\omega_z\omega_x &= -\beta_y\omega_y + A_y(t) \\ \dot{\omega}_z - \frac{I_x - I_y}{I_z}\omega_x\omega_y &= -\beta_z\omega_z + A_z(t). \end{aligned} \tag{4}$$

On account of the second terms on the left hand sides these equations are non-linear in general.

In the case of the sphere (4) become linear and the normalized auto-correlation function of $Y_{jm}(\theta(t),\phi(t))$ is given by[3]

$$\frac{\langle Y_{jm}^*(\theta(t),\phi(t))\, Y_{jm}(\theta(0),\phi(0))\rangle}{\langle Y_{jm}^*(\theta(0),\phi(0))\, Y_{jm}(\theta(0),\phi(0))\rangle}$$
$$= \exp\left\{-j(j+1)\left[\frac{kT}{I}I^{(2)}(t) + \left(\frac{kT}{I}\right)^2 I_2^{(4)}(t) + \left(\frac{kT}{I}\right)^3\left(I_3^{(6)}(t) + 4I_4^{(6)}(t)\right) + \left(\frac{kT}{I}\right)^4\left(I_4^{(8)}(t) + 8I_5^{(8)}(t) + [-4j(j+1)+16]I_7^{(8)}(t) + [-10j(j+1)+38]I_8^{(8)}(t)\right)+\cdots\right]\right\}. \tag{5}$$

The values of the $I(t)$'s given in ref. 3 show that $I^{(2)}(t)$ is proportional to β^{-2}. $I_2^{(4)}(t)$ is proportional to β^{-4}, etc., so the exponent is a power series in γ defined by (2). On putting $j = 1$, $m = 0$ in (5), expanding the

exponential in powers of γ and substituting into (1) we obtain (3).

Equations (4) become linear also for the rotating needle. It is found that the normalized autocorrelation function of $Y_{jm}(\theta(t), \phi(t))$ is now

$$\exp\left\{-j(j+1)\left[\frac{kT}{I} I^{(2)}(t) + \left(\frac{kT}{I}\right)^2 2I_2^{(4)}(t) + \left(\frac{kT}{I}\right)^3 (4I_3^{(6)}(t) + 20I_4^{(6)}(t)) + \cdots\right]\right\} \quad (6)$$

On putting j = 1, m = 0 and substituting into (1) we find agreement with Sack's continued fraction expression for $\alpha(\omega)$.

We now report some unpublished results found in collaboration with Professors G. W. Ford and J. T. Lewis for the case of a molecule with no particular symmetry. If the second terms on the left hand sides of (4) were absent, the stationary solutions would be the Ornstein-Uhlenbeck processes

$$2^{1/2}\beta_x^{3/2}\left(\frac{kT}{I_x\beta_x^2}\right)^{1/2}\int_{-\infty}^{t} e^{-\beta_x(t-s)} A_x(s)\,ds, \quad (7)$$

etc.. These are Gaussian random variables. Let us write (7) as $\epsilon\,\omega_x^{(1)}(t)$ with

$$\epsilon = \frac{(kT)^{1/2}}{(I_x I_y I_z \beta_x^2 \beta_y^2 \beta_z^2)^{1/6}}.$$

We suppose that $\frac{kT}{I_x\beta_x^2}$, $\frac{kT}{I_y\beta_y^2}$, $\frac{kT}{I_z\beta_z^2}$ are small compared with unity, so that ϵ^2 is also small compared with unity, and we express the solutions of the complete equations (4) as

$$\omega_x(t) = \epsilon\,\omega_x^{(1)}(t) + \epsilon^2\omega_x^{(2)}(t) + \epsilon^3\omega_x^{(3)}(t) + \cdots,$$

etc.. On substituting into (4) we find that

$$\omega_x^{(2)}(t) = \frac{I_y - I_z}{I_x}\int_{-\infty}^{t} e^{-\beta_x(t-t_1)}\,\omega_y^{(1)}(t)\,\omega_z^{(1)}(t_1)\,dt_1, \quad (8)$$

etc., with more complicated expressions for $\omega_x^{(3)}(t)$, $\omega_x^{(4)}(t)$ etc.. On account of the product $\omega_y^{(1)}(t)\,\omega_z^{(1)}(t_1)$ in (8), $\omega_x^{(2)}(t)$ is not Gaussian and so $\omega_x(t)$, $\omega_y(t)$, $\omega_z(t)$ are not Gaussian.

Since an asymmetric body has three rotational degrees of freedom, we examine the mean value of $D^j_{mm'}(\alpha(t), \beta(t), \gamma(t))$ defined by Rose[4]. This is the mm'-matrix element of an operator $R(t)$ satisfying

$$\frac{d\langle R(t)\rangle}{dt} = (\epsilon^2\zeta_2(t) + \epsilon^4\zeta_4(t) + \cdots)\langle R(t)\rangle, \quad (9)$$

where

$$\epsilon^2\zeta_2(t) = -\frac{kT}{I_x\beta_x}(1-e^{-\beta_x t})J_x^2 - \frac{kT}{I_y\beta_y}(1-e^{-\beta_y t})J_y^2 - \frac{kT}{I_z\beta_z}(1-e^{-\beta_z t})J_z^2$$

and J_x, J_y, J_z are 2j+1-dimensional representatives of the components of angular momentum divided by $\hbar$. The values of $\epsilon^4\zeta_4(t)$, etc. are too lengthy to reproduce here. On account of the time dependence of ζ_2, ζ_4, etc. equation (9) cannot be integrated directly. However it can be integrated indirectly by a method used by Bogoliubov and Mitropolsky[5]. To obtain some insight into the results of the calculations we neglect products of $\frac{kT}{I_x\beta_x^2}$, $\frac{kT}{I_y\beta_y^2}$, $\frac{kT}{I_z\beta_z^2}$ and let j = 1, m = m' = 0. Then, if $\theta(t)$ is the angle between the orientation of the z-axis at time t and time zero,

$$\langle\cos\theta(t)\rangle = \left\{1 + \frac{kT}{I_x\beta_x^2}(1-e^{-\beta_x t}) + \frac{kT}{I_y\beta_y^2}(1-e^{-\beta_y t}) + \frac{kT}{I_z\beta_z^2}(1-e^{-\beta_z t})\right\}\exp\left[-t\left(\frac{kT}{I_x\beta_x} + \frac{kT}{I_y\beta_y} + \right.\right.$$

COMPLEX POLARIZABILITIES AND CORRELATION TIMES

The same methods may be employed to calculate complex polarizabilities. Writing

$$\alpha(\omega) = \alpha'(\omega) - i\alpha''(\omega)$$

denoting by μ the electric moment of a polar molecule and putting

$$A = 1 + 2\gamma + \frac{9}{2}\gamma^2 + \frac{95}{9}\gamma^3 + \cdots$$
$$B = 2\gamma\beta\left(1 + \tfrac{1}{2}\gamma + \tfrac{7}{12}\gamma^2 + \tfrac{25}{36}\gamma^3 + \cdots\right),$$

we have for the spherical model

$$\frac{\alpha'(\omega)}{\frac{\mu^2}{3kT}} = 1 - A\left[\frac{\omega^2}{B^2+\omega^2} - \gamma\frac{2\omega^2}{(\beta+B)^2+\omega^2} - \gamma^2\left(\frac{4\beta(\beta+B)\omega^2}{[(\beta+B)^2+\omega^2]^2} + \frac{2\omega^2}{(\beta+B)^2+\omega^2} - \frac{\frac{3}{2}\omega^2}{(2\beta+B)^2+\omega^2}\right)\right.$$
$$-\gamma^3\left(\frac{6\beta^2(\beta+B)^2\omega^2 - 2\beta^2\omega^4}{[(\beta+B)^2+\omega^2]^3} + \frac{8\beta(\beta+B)\omega^2}{[(\beta+B)^2+\omega^2]^2} + \frac{2\omega^2}{(\beta+B)^2+\omega^2}\right.$$
$$\left.\left. + \frac{3\beta(2\beta+B)\omega^2}{[(2\beta+B)^2+\omega^2]^2} + \frac{\frac{17}{9}\omega^2}{(3\beta+B)^2+\omega^2}\right) - \cdots\right],$$

$$\frac{\alpha''(\omega)}{\frac{\mu^2}{3kT}} = A\left[\frac{B\omega}{B^2+\omega^2} - \gamma\frac{2(\beta+B)\omega}{(\beta+B)^2+\omega^2}\right.$$
$$-\gamma^2\left(\frac{2\beta[(\beta+B)^2-\omega^2]\omega}{[(\beta+B)^2+\omega^2]^2} + \frac{2(\beta+B)\omega}{(\beta+B)^2+\omega^2} - \frac{(3\beta+\frac{3}{2}B)\omega}{(2\beta+B)^2+\omega^2}\right)$$
$$-\gamma^3\left(\frac{2\beta^2[(\beta+B)^3\omega - 3(\beta+B)\omega^3]}{[(\beta+B)^2+\omega^2]^3} + \frac{4\beta[(\beta+B)^2-\omega^2]\omega}{[(\beta+B)^2+\omega^2]^2}\right.$$
$$\left. + \frac{2(\beta+B)\omega}{(\beta+B)^2+\omega^2} + \frac{\frac{3}{2}\beta[(2\beta+B)^2-\omega^2]\omega}{[(2\beta+B)^2+\omega^2]^2}\right.$$
$$\left.\left. + \frac{(\frac{17}{3}\beta + \frac{17}{9}B)\omega}{(3\beta+B)^2+\omega^2}\right) - \cdots\right].$$

For the needle molecule we put

$$C = 1 + 2\gamma + 7\gamma^2 + \frac{274}{9}\gamma^3 + \cdots$$
$$D = 2\gamma\beta\left(1 + \gamma + \tfrac{8}{3}\gamma^2 + \cdots\right),$$

and then

$$\frac{\alpha'(\omega)}{\frac{\mu^2}{3kT}} = 1 - C\left[\frac{\omega^2}{D^2+\omega^2} - \gamma\frac{2\omega^2}{(\beta+D)^2+\omega^2} - \gamma^2\left(\frac{8\beta(\beta+D)\omega^2}{[(\beta+D)^2+\omega^2]^2} + \frac{4\omega^2}{(\beta+D)^2+\omega^2} - \frac{\omega^2}{(2\beta+D)^2+\omega^2}\right)\right.$$
$$-\gamma^3\left(\frac{24\beta^2(\beta+D)^2\omega^2 - 8\omega^4\beta^2}{[(\beta+D)^2+\omega^2]^3} + \frac{40\beta(\beta+D)\omega^2}{[(\beta+D)^2+\omega^2]^2} + \frac{6\omega^2}{(\beta+D)^2+\omega^2}\right.$$
$$\left.\left. + \frac{4\omega^2}{(2\beta+D)^2+\omega^2} + \frac{\frac{4}{9}\omega^2}{(3\beta+D)^2+\omega^2}\right) - \cdots\right],$$

$$\frac{\alpha''(\omega)}{\frac{\mu^2}{3kT}} = C\left[\frac{D\omega}{D^2+\omega^2} - \gamma\frac{2(\beta+D)\omega}{(\beta+D)^2+\omega^2} - \gamma^2\left(\frac{4\beta[(\beta+D)^2-\omega^2]\omega}{[(\beta+D)^2+\omega^2]^2} + \frac{4(\beta+D)\omega}{(\beta+D)^2+\omega^2}\right.\right.$$
$$\left.\left. - \frac{2(\beta+D)\omega}{(2\beta+D)^2+\omega^2}\right)\right.$$
$$-\gamma^3\left(\frac{8\beta^2[(\beta+D)^3\omega - 3(\beta+D)\omega^3]}{[(\beta+D)^2+\omega^2]^3} + \frac{20\beta[(\beta+D)^2-\omega^2]\omega}{[(\beta+D)^2+\omega^2]^2}\right.$$
$$\left. + \frac{4(2\beta+D)\omega}{(2\beta+D)^2+\omega^2} + \frac{6(\beta+D)\omega}{(\beta+D)^2+\omega^2} + \frac{\frac{4}{9}(3\beta+D)\omega}{(3\beta+D)^2+\omega^2}\right) - \cdots\Big].$$

We can in a similar manner obtain the correlation time τ_j related to the spherical harmonic $Y_{jm}(\theta(t), \phi(t))$. For the spherical model

$$\tau_j = \frac{1}{j(j+1)\gamma\beta}\left[1 + \gamma\left\{-\tfrac{1}{2} + j(j+1)\right\} + \gamma^2\left\{-\tfrac{1}{3} + \tfrac{3}{4}j(j+1) - \tfrac{1}{2}j^2(j+1)^2\right\}\right.$$
$$\left. + \gamma^3\left\{-\tfrac{35}{72} + \tfrac{23}{18}j(j+1) - \tfrac{9}{8}j^2(j+1)^2 + \tfrac{5}{12}j^3(j+1)^3\right\} + \cdots\right].$$

The first term is the Debye correlation time. By a diffusion equation calculation Hubbard[6] obtained the last equation as far as the γ^2-term in the series. For a rotating needle

$$\tau_j = \frac{1}{j(j+1)\gamma\beta}\left[1 + \gamma\left\{-1 + j(j+1)\right\} + \gamma^2\left\{-\tfrac{5}{3} + \tfrac{3}{2}j(j+1) - \tfrac{1}{2}j^2(j+1)^2\right\}\right.$$

CONCLUSION

The autocorrelation function of $D^{j}_{mm'}(\alpha(t), \beta(t), \gamma(t))$ has been calculated up to terms of second order in $\frac{kT}{I_x \beta_x^2}$, $\frac{kT}{I_y \beta_y^2}$, $\frac{kT}{I_z \beta_z^2}$ for the rotational Brownian motion of an asymmetric polar molecule in a non-polar solvent under the assumptions that the frictional torque about a principal axis of inertia is proportional to the component of angular velocity about that axis and that the influence of the fields of the other polar molecules is negligible. The calculations may be extended to orders higher than the second. For the particular cases of spherical and needle molecules correlation times for $Y_{j,m}(\theta(t), \phi(t))$, and complex polarizabilities are expressed in terms of series in $kT/I\beta^2$.

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